

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 156 052 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

21.11.2001 Bulletin 2001/47

(51) Int Cl.7: **C07F 7/14**

(21) Application number: **01304327.8**

(22) Date of filing: **15.05.2001**

(84) Designated Contracting States:

**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR**

Designated Extension States:

AL LT LV MK RO SI

(30) Priority: **15.05.2000 JP 2000142128**

(71) Applicant: **SHIN-ETSU CHEMICAL CO., LTD.**
Chiyoda-ku Tokyo (JP)

(72) Inventors:

- **Tonomura, Yoichi,**
Specialty Chemicals Res. Centre
Kubiki-mura, Nakakubiki-gun, Niigata-ken (JP)

- **Kubota, Tohru, Specialty Chemicals Res. Centre**
Kubiki-mura, Nakakubiki-gun, Niigata-ken (JP)
- **Endo, Mikio, Specialty Chemicals Res. Centre**
Kubiki-mura, Nakakubiki-gun, Niigata-ken (JP)

(74) Representative: **Stoner, Gerard Patrick et al**
MEWBURN ELLIS
York House
23 Kingsway
London WC2B 6HP (GB)

(54) **Preparation of halopropyldimethylchlorosilanes**

(57) A halopropyldimethylchlorosilane is prepared by reacting dimethylchlorosilane with an allyl halide in the presence of an iridium catalyst. The reaction is effected in the presence of an internal olefin compound,

typically 1,5-cyclooctadiene. The internal olefin compound suppresses deactivation of the iridium catalyst during reaction. Using a smaller amount of the iridium catalyst, the process produces the halopropyldimethylchlorosilane in high yields.

BEST AVAILABLE COPY

EP 1 156 052 A2

Description

[0001] This invention relates to a process for preparing halopropyldimethylchlorosilanes which are useful as intermediates for the synthesis of various silane coupling agents and as modifiers for silicone fluid.

BACKGROUND

[0002] Halopropylchlorosilane compounds are used as intermediates for the synthesis of various silane coupling agents and as modifiers for silicone fluid. These compounds are generally synthesized by reacting allyl halides with hydrogenchlorosilane compounds such as trichlorosilane, methyldichlorosilane and dimethylchlorosilane. In the reaction, platinum and rhodium-containing compounds are used as the catalyst.

[0003] The process of preparing halopropylchlorosilane compounds using platinum-containing compounds is disclosed, for example, in USP 2,823,218, 3,814,730, 3,715,334, 3,516,946, 3,474,123, 3,419,593, 3,220,922, 3,188,299, 3,178,464, and 3,159,601. The process using rhodium-containing compounds is disclosed, for example, in USP 3,296,291 and 3,564,266. Most of these processes use trichlorosilane and methyldichlorosilane as the hydrogenchlorosilane compound.

[0004] The use of trichlorosilane and methyldichlorosilane as the hydrogenchlorosilane compound is described in many patents as noted above. However, the use of dimethylchlorosilane is described in few patents because of low selectivity of reaction, although the end products, halopropyldimethylchlorosilane compounds are useful as intermediates for the synthesis of various silane coupling agents and as modifiers for silicone fluid. Uniquely Japanese Patent No. 2938731 is directed to the preparation of a halopropyldimethylchlorosilane compound using an iridium complex. This process, however, suffers from the problem that a large amount of the expensive iridium complex must be used as the catalyst, and is thus not regarded as advantageous in practicing on an industrial scale.

[0005] An object of the invention is to provide a simple process suitable for preparing halopropyldimethylchlorosilanes on an industrial scale.

[0006] The invention pertains to a process for preparing a halopropyldimethylchlorosilane of the following general formula (1):



wherein X is chlorine, bromine or iodine, by reacting dimethylchlorosilane with an allyl halide of the following general formula (2):

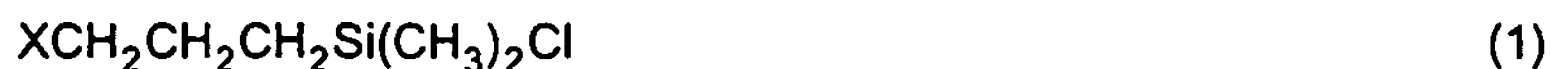


wherein X is as defined above in the presence of an iridium catalyst. Quite unexpectedly, the inventor has found that deactivation of the iridium catalyst during reaction is suppressed by adding an internal olefin compound of the following general formula (3) to the reaction system.



Herein R^1 and R^2 each are a monovalent hydrocarbon group having 1 to 10 carbon atoms; R^1 and R^2 may join to form a ring system. R^3 and R^4 are hydrogen or monovalent hydrocarbon group having 1 to 10 carbon atoms. Even when the amount of the iridium catalyst used is reduced, the halopropyldimethylchlorosilane is produced in high yields.

[0007] The invention provides a process for preparing a halopropyldimethylchlorosilane of the general formula (1):

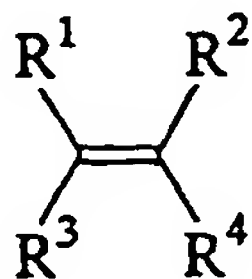


by reacting dimethylchlorosilane with an allyl halide of the general formula (2):



(2)

in the presence of an iridium catalyst, characterized in that the reaction is effected in the presence of a compound of the general formula (3):



(3)

Herein, X and R¹ to R⁴ are as defined above.

DETAILED DESCRIPTION; PREFERRED AND OPTIONAL FEATURES

[0008] The starting reactant to be reacted with dimethylchlorosilane is an allyl halide of the general formula (2):



(2)

wherein X is chlorine, bromine or iodine. Specifically, the allyl halides are allyl chloride, allyl bromide and allyl iodide. The amount of the allyl halide used is not critical although it is preferred to use 0.5 to 2.0 mol, especially 0.9 to 1.2 mol of allyl halide per mol of dimethylchlorosilane.

[0009] The iridium catalyst used herein encompasses iridium salts and iridium complexes. Exemplary iridium salts are iridium trichloride, iridium tetrachloride, chloroiridic acid, sodium chloroiridate and potassium chloroiridate. The iridium complexes include those represented by the following general formula (4):

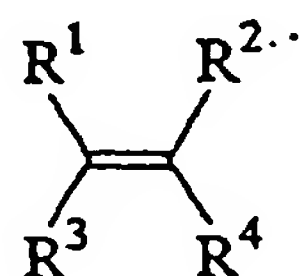


(4)

wherein R is a diene compound and Y is chlorine, bromine or iodine. Illustrative examples of the iridium complexes of formula (4) include di-μ-chlorobis(μ-1,5-hexadiene)-diiridium, di-μ-bromobis(μ-1,5-hexadiene)-diiridium, di-μ-iodobis(μ-1,5-hexadiene)-diiridium, di-μ-chlorobis(μ-1,5-cyclooctadiene)-diiridium, di-μ-bromobis(μ-1,5-cyclo-octadiene)-diiridium, di-μ-iodobis(μ-1,5-cyclooctadiene)-diiridium, di-μ-chlorobis(μ-2,5-norbornadiene)-diiridium, di-μ-bromobis(μ-2,5-norbornadiene)-diiridium, and di-μ-iodobis(μ-2,5-norbornadiene)-diiridium.

[0010] No particular limit is imposed on the blending ratio of the iridium catalyst although it is preferred to use the iridium catalyst in such amounts as to give 0.000001 to 0.01 mol, especially 0.00001 to 0.001 mol of iridium atom per mol of dimethylchlorosilane. Less than 0.000001 mol of the catalyst may fail to exert significant effect whereas more than 0.01 mol of the catalyst may not provide reaction promoting effects corresponding to the increment of the catalyst.

[0011] The reaction is carried out in the presence of internal olefin compound of the formula (3).



(3)

Herein R¹ and R² each are a monovalent hydrocarbon group having 1 to 10 carbon atoms, or R¹ and R², taken together, may form a ring. R³ and R⁴ each are hydrogen or a monovalent hydrocarbon group having 1 to 10 carbon atoms. When hydrocarbon, R³ and/or R⁴ may or may not be in a ring system. The compound is typically aliphatic or alicyclic. R¹ and R² may be cis or trans. The compound may have one or more unsaturations, provided that at least one is not at a chain end. Preferred compounds are linear, branched and cyclic (optionally polycyclic) alkenes. Examples include 2-hexene, 3-hexene, 2-heptene, 2-octene, 4-octene, 2-decene, 5-decene, cyclopentene, cyclohexene, 2-norbornene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, 4-vinyl-1-cyclohexene, 1,5-cyclooctadiene, 2,5-norbornadiene, 5-vinyl-2-norbornene, and terpenes e.g. limonene. From the reactivity and catalyst stability standpoints, 1,5-cyclooctadiene

is most preferred.

[0012] No particular limit is imposed on the amount of the compound of formula (3) used although it is preferred to use 0.5 to 10,000 mol, especially 1 to 1,000 mol of the compound per mol of iridium atom in the iridium catalyst. Less than 0.5 mol of the compound may fail to exert the desired effects whereas more than 10,000 mol of the compound may fail to provide effects corresponding to that amount and cause more by-products to form, resulting in reduced yield and purity.

[0013] The reaction will proceed in a solventless system although a solvent is used if desired. Useful solvents include hydrocarbon solvents such as pentane, hexane, cyclohexane, heptane, octane, isooctane, benzene, toluene, and xylene; ether solvents such as diethyl ether, tetrahydrofuran, and dioxane; ester solvents such as ethyl acetate and butyl acetate; aprotic polar solvents such as acetonitrile; and chlorinated hydrocarbon solvents such as dichloromethane and chloroform, which may be used alone or in admixture of two or more.

[0014] The reaction temperature is not critical. A temperature in the range of about 0°C to about 200°C, especially about 10°C to about 100°C is preferred when reaction is effected under atmospheric pressure or under pressure. The reaction time is usually from about 1 hour to about 10 hours.

[0015] According to the invention, the above-described reaction yields a halopropyldimethylchlorosilane of the general formula (1):



wherein X is chlorine, bromine or iodine. Specifically, the silanes are 3-chloropropyldimethylchlorosilane, 3-bromopropyldimethylchlorosilane, and 3-iodopropyldimethylchlorosilane.

EXAMPLE

[0016] Examples of the invention are given below by way of illustration and not by way of limitation.

Example 1

[0017] A flask equipped with a stirrer, reflux condenser, dropping funnel and thermometer was charged with 153.0 g (2.0 mol) of allyl chloride, 67.2 mg (0.0001 mol) of di- μ -chlorobis(μ -1,5-cyclooctadiene)diiridium, and 0.43 g (0.004 mol) of 1,5-cyclooctadiene and heated at 35°C. Once the internal temperature was stabilized, 189.2 g (2.0 mol) of dimethylchlorosilane was added dropwise over 6 hours. During the dropwise addition, the reaction mixture continued to be exothermic. After the completion of dropwise addition, the reaction solution was stirred for one hour at 40°C. The reaction solution was distilled, collecting 317.2 g of a fraction having a boiling point of 84°C/6.7 kPa, which was 3-chloropropyldimethylchlorosilane (yield 92.7%).

Example 2

[0018] A flask equipped with a stirrer, reflux condenser, dropping funnel and thermometer was charged with 153.0 g (2.0 mol) of allyl chloride, 67.2 mg (0.0001 mol) of di- μ -chlorobis(μ -1,5-cyclooctadiene)diiridium, and 0.33 g (0.004 mol) of cyclohexene and heated at 35°C. Once the internal temperature was stabilized, 189.2 g (2.0 mol) of dimethylchlorosilane was added dropwise over 6 hours. During the dropwise addition, the reaction mixture continued to be exothermic. After the completion of dropwise addition, the reaction solution was stirred for one hour at 40°C. The reaction solution was analyzed by gas chromatography, finding a conversion of 81.5%.

Comparative Example 1

[0019] Reaction was effected as in Example 1 except that 1,5-cyclooctadiene was omitted. The reaction mixture ceased to be exothermic after approximately 50% of the predetermined amount of dimethylchlorosilane had been added dropwise. The final conversion was as low as 50.5%.

Example 3

[0020] A flask equipped with a stirrer, reflux condenser, dropping funnel and thermometer was charged with 153.0 g (2.0 mol) of allyl chloride, 1.9 g (0.0002 mol) of a 2 wt% butanol solution of chloroiridic acid, and 2.2 g (0.02 mol) of 1,5-cyclooctadiene and heated at 35°C. Once the internal temperature was stabilized, 189.2 g (2.0 mol) of dimethyl-

chlorosilane was added dropwise over 6 hours. During the dropwise addition, the reaction mixture continued to be exothermic. After the completion of dropwise addition, the reaction solution was stirred for one hour at 40°C. The reaction solution was analyzed by gas chromatography, finding a conversion of 73.9%.

Comparative Example 2

[0021] Reaction was effected as in Example 3 except that 1,5-cyclooctadiene was omitted. After one hour of stirring at 40°C, the conversion was as low as 8.3%.

[0022] There has been described a process for the preparation of a halopropyldimethylchlorosilane compound from dimethylchlorosilane and an allyl halide in the presence of an iridium catalyst wherein an internal olefin compound is added to the reaction system for suppressing deactivation of the iridium catalyst during reaction, whereby the halopropyldimethylchlorosilane is produced in high yields despite a smaller amount of the iridium catalyst. The invention enables the efficient production of halopropyldimethylchlorosilane on an industrial scale.

[0023] Japanese Patent Application No. 2000-142128 is incorporated herein by reference.

[0024] Although some preferred embodiments have been described many modifications and variations may be made thereto in light of the above teachings. It is therefore to be understood that the invention may be practiced otherwise than as specifically described in the Examples.

Claims

1. A process for preparing halopropyldimethylchlorosilane of the following general formula (1):



wherein X is chlorine, bromine or iodine, by reacting dimethylchlorosilane with allyl halide of the following general formula (2):



wherein X is as defined above in the presence of iridium catalyst, characterized in that the reaction is effected in the presence of compound of the following general formula (3):



wherein R¹ and R² are monovalent C₁₋₁₀ hydrocarbon groups which may join to form a ring system and R³ and R⁴ are hydrocarbon or monovalent hydrocarbon group having 1 to 10 carbon atoms.

2. A process of claim 1 wherein the iridium catalyst is a compound of the following general formula (4):



wherein R is a diene ligand and Y is chlorine, bromine or iodine.

3. A process of claim 1 or 2 in which the compound of formula (3) is aliphatic or alicyclic.

4. A process of claim 1 or 2 wherein the compound of formula (3) is 1,5-cyclooctadiene.

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 156 052 A3

(12)

EUROPEAN PATENT APPLICATION

(88) Date of publication A3:
17.09.2003 Bulletin 2003/38

(51) Int Cl.7: **C07F 7/14**

(43) Date of publication A2:
21.11.2001 Bulletin 2001/47

(21) Application number: **01304327.8**

(22) Date of filing: **15.05.2001**

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR**
Designated Extension States:
AL LT LV MK RO SI

- Kubota, Tohru, Specialty Chemicals Res. Centre
Kubiki-mura, Nakakubiki-gun, Niigata-ken (JP)
- Endo, Mikio, Specialty Chemicals Res. Centre
Kubiki-mura, Nakakubiki-gun, Niigata-ken (JP)

(30) Priority: **15.05.2000 JP 2000142128**

(74) Representative: Stoner, Gerard Patrick et al
MEWBURN ELLIS
York House
23 Kingsway
London WC2B 6HP (GB)

(71) Applicant: **SHIN-ETSU CHEMICAL CO., LTD.**
Chiyoda-ku Tokyo (JP)

(72) Inventors:
• Tonomura, Yoichi,
Specialty Chemicals Res. Centre
Kubiki-mura, Nakakubiki-gun, Niigata-ken (JP)

(54) **Preparation of halopropyldimethylchlorosilanes**

(57) A halopropyldimethylchlorosilane is prepared by reacting dimethylchlorosilane with an allyl halide in the presence of an iridium catalyst. The reaction is effected in the presence of an internal olefin compound, typically 1,5-cyclooctadiene. The internal olefin com-

pound suppresses deactivation of the iridium catalyst during reaction. Using a smaller amount of the iridium catalyst, the process produces the halopropyldimethylchlorosilane in high yields.

EP 1 156 052 A3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 01 30 4327

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
D,A	DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; KUBOTA, TOORU ET AL: "Preparation of (halopropyl)dimethylchlorosilane and catalysts used in the preparation" retrieved from STN Database accession no. 123:340390 CA XP002248253 * abstract * & JP 02 938731 B (SHINETSU CHEM IND CO, JAPAN) 25 August 1999 (1999-08-25)	1	C07F7/14
E	EP 1 201 671 A (CONSORTIUM FÜR ELECTROCHEMISCHE INDUSTRIE GMBH) 2 May 2002 (2002-05-02) * the whole document *	1-4	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			C07F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 18 July 2003	Examiner Rinkel, L
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 01 30 4327

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

18-07-2003

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 2938731	B	16-05-1995	JP 2938731 B2	25-08-1999
			JP 7126271 A	16-05-1995
EP 1201671	A	02-05-2002	DE 10053037 C1	17-01-2002
			CN 1351015 A	29-05-2002
			EP 1201671 A1	02-05-2002
			JP 2002179684 A	26-06-2002
			PL 350308 A1	06-05-2002
			US 2002052520 A1	02-05-2002

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☒ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.